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SOLVENT EFFECTS ON ACID BASE EQUILIBRIA

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by

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ABSTRACT

The fundamental principles of acid-base equilibria are discussed in terms of the basic thermodynamics, the methods of studying equilibria and the recent methods of determination of equilibrium constants using titrimetry. The definitions of acidity and basicities are discussed. Solvent properties categorized by autoprotolysis constants, solvation ability, dielectric constants and molecular structures are shown to influence the shapes of the titration curves, the sharpness of the break points, leveling effects and differentiating abilities of mixed solvents. The dielectric's influence on dissociation constants, and homoconugation are discussed. The charge type of dissociating species, influence the dissociation constants. The moleuclar properties of the solvent influence the titration behaviour.

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EFFETS DES SOLVANTS SUR LES ÉQUILIBRES ACIDES-BASES

par

C.W. Angle*

RÉSUMÉ

On étudie les principes fondamentaux des équilibres acides-bases en fonction de la thermodynamique fondamentale, des méthodes d'étude des équilibres, et des méthodes récentes de détermination des constantes d'équilibre au moyen de la titrimétrie. On commente les définitions d'acidité et de basicité. On démontre que les propriétés des solvants catégorisées par les constantes d'autoprotolyse, la capacité de solvation, les constantes diélectriques et les structures moléculaires influencent la configurations des courbes de titrage, la netteté des points de rupture, les effets de nivellement et les capacités de différenciation des solvants mixtes. On discute de l'influence du diélectrique sur les constantes de dissociation et sur l'homoconjugation. Le type de charge des espèces qui se dissocient influence les constantes de dissociation. Les propriétés moléculaires du solvant influencent le déroulement du titrage.

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INTRODUCTION AND SCOPE

Acid base equilibria are affected by various properties of solvents. In the recovery of fossil fuels,the interactions of various indigenous organic and inorganic acids and bases with water and various organic solvents, are part of processing operations. Coal as an organic rock is mixed with vater and electrolytes,as well as acids,bases ,and polymers in recovery processes. In solvolytic extractions, it participates in acid base equilibria with solvents of wide acid base character. Crude oils undergo similar treatments.

In the interest of these applications, it becomes necessary to understand the fundamentals of acid-base equilibria, so that meaningful experiments could be designed for scale up operations. Acids and bases, which are only slightly dissociated in water, could be studied in organic solvents. The choice of solvents then becomes important depending on the desired goal. Understanding the concept of acids, bases, and the nature and role of different solvents in each system is essential to comphehending the effects of solvents on the acid base equilibrium.

Recent research papers address the comparisons of methods of calculating the pKa's ,errors, relative acidity and basicity of various solvents in determination of relative acid or basic strengths of solutes, and structural effects of the molecules on equilibria,(1-17). In the interest of brevity electrode reactions (18), errors (14),theory of transfer activity coefficients and related energetics (2), titration anomalies (19), and the effects of mixed solvents (including water contamination) on titration curves (18), have not been addressed. Emphasis has been placed on the fundamentals,the properties of solvents (especially the dielectric constants), and the molecular properties of solvents and solutes as they influence equilibrium data.

Kratochvil (17,20) has published a series of reviev articles on the titrations in nonaqueous solvents. These articles are guides to the basic literature on the subject. Details on acid base equilibria appear in E.J. King (21), and are not repeated here. The chemistry of nonaqueous solvents is revieved by Lagovski (22), and titrations from a practical viewpoint are covered in a text by Kucharsky and Safarik (18), and Fritz

(23). The basic concepts of acid-base behaviour in aqueous and nonaqueous solvents have been included in many analytical textbooks (24,25,26).

FUNDAMENTALS

Concept of Equilibrium

Equilibrium could be approached either from a 'kinetics' or 'energetics' point of view. From a kinetics point of view equilibrium can be described as a dynamic balance of forward and reverse rate of reactions of given reactants. From an energetics point of view equilibrium can be described as a state of maximum stability. The system moves towards equilibrium state spontaneously and if removed from this state by a stressor the disturbed system will readjust to another equilibrium state to accomodate this. In this paper equilibrium is discussed from an energetics viewpoint.

The equilibrium composition is the composition of reactants and products that correspond to the lowest point in a free energy curve. At this point "conversion of small quantities of reactants to products causes no change in free energy" (27) i.e. the slope of the free energy curve is zero. In summary the following relations hold:

$$\Delta G_r^\circ = -RT \ln K_{th} = -RT \ln \frac{a_c^c \, a_D^d}{a_B^b \, a_a^a} = -RT \ln Q$$

where ΔG_r° is the standard free energy change of the reaction, a is the activity of reacting species, Q is the quotient of products over reactants and Kth is the thermodynamic equilibrium constant for a standard reaction, while R,T are the gas constants and temperature respectively (1).

In terms of potentiometry, if a reversible electron transfer reaction is considered, the potential acquired by an electrode in contact with an equilibrium mixture of A,B,C,D,....,is expressed in the following relationship:

$$aA + bB + ... \; ze^- \quad cC + dD ....$$

$$E = E_T^\circ + \frac{RT}{nF} \ln [(C)^c (D)^d / (A)^a (B)^b]$$

where E_T° is the standard electrode potential when all species are unit activity. For proton transfer(18), the Nerst equation holds as well:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{Acid}{Base}$$

$$-\Delta G^\circ = nF E^\circ_{cell}$$

n = # of electrons, F = Faraday's constant, E°_{cell}= Potential of cell.

Both the size of K and the concentration of species (reactants and products) determine the direction of the reaction. Also temperature, pressure, and/or catalyst would affect the equilibrium condition.

Methods of Studying Equilibria

Equilibria have been studied by a variety of techniques (28): 1. UV & Vis spectroscopy and photometry, 2. spectroscopy which include IR, Raman, NMR, ESR, mossbauer, refractometry light scattering, ultrasonic absorption, spectropolarimetry, 3. distribution methods (such as liquid liquid partition, solubility, ionexchange),chromatography,(gas,liquid and thin layer), 4. electrochemical methods such as potentiometry,also polarography, anodic stripping voltametry and conductivity, 5. direct colorimetry, 6. calorimetry such as direct and thermometric titration calorimetry.

The study of medium and solvent effects on the systems have entailed many of the above techniques, however recent papers have emphasised conductometric and potentiometric (6) spectrophotometric (31) and voltammetric techniques (4,15). Emphasis has been placed on the effects on acidity constants Ka (6). Some have looked at the shapes of titration curves and others compared their data with theory (11-13). The data described the nature of the solvent or the stoichiometry of the system or in the case of the titration curves the design of the system, for the particular situation. Theoretical plots served as a guide to the selection of the medium for the systems of concern.

Equilibrium is tested by measuring redox potential,absorbance or pH of the sample with variation of concentration of one or more reactants or products. The observed concentration is compared with that expected from the theoretical equilibrium expressions. Stoichiometry is indicated from the break points in a signal versus concentration curve, especially in the case of potentiometric methods. From equivalence concentrations of known titrants the equilibrium constants can be calculated using one of many techniques(28,29). However,the absence of detectable changes in the concentration of reactants or products is not necessarily definite evidence for equilibrium since in some cases equilibrium development is slow. Potentiometry is most accurate for potentials that originate from oxidation reduction and ionic gradients across a membrane. Titration techniques are good for systems that reach equilibrium rapidly.

Determination of Equilibrium Constants

Rosotti (30) has described a variety of methods for calculation of equilibrium constants from concentration data. The recent literature either modifies or uses classical methods with the help of the computer to perform the iterative operations.

Papanastasiou et al (10) determined a series of thermodynamic acidity constants in ternary water/dioxane/methanol mixtures. A set of monocarboxlyic acid pKa's were calculated using an iterative method as follows:

$$pKa = f(1/D)$$

$$dpKa/d(1/D) = (e^2/2kTln10)Q$$

where D is the dielectric constant, and Q is the reciprocal harmonic mean radius of the ions taking part in the equilibrium. Straight line plots were found. The drawback is that the dielectric constant of ternary mixtures is not easily found. However an extended interpolation formula can be used to predict the pKa of acids in any ternary solvent without knowledge of the dielectric constant. They concluded that non-electrostatic solute-solvent interactions change from one solvent series to another.

Velinov & Budevsky (15) proposed a least-squares method for calculating KsH, the ionic product of nonaqueous amphiprotic solvents using potentiometric data from the titration of any weak acid with a weak base.

The acid base constant is obtained at the same time. Unlike the classical method no strong acid or base is necessary for determining KsH. The difficulty in evaluating ionic strength of nonaqueous solution is therefore omitted.

An alternative iterative method was published by Castello et al (12) for the pKa determination of a weak acid using strong base in aqueous media; from only one point on the titration curve the pKa could be calculated.

Halliday et al (11) compared equivalence points determined on a weak acid and strong base titration u ing three methods: a photometric method with normal and Higuchi plots, potentiometric methods using point of inflection, and Gran plots (29). These values were compared to values from theoretical curves obtained by a numerical Newton Rhapson iteration method. They were able to duplicate their results with theoretical curves. The photometric and potentiometric titration curves gave similar results. Higuchi and Gran linear intercept methods gave a lover result. One can use Gran plots to determine the pKa.

Petho and Burger (16) used half neutralisation points from the potentiometric titration curves which do not show realistic inflection points at the end point. They were able to show that weak bases measurable only in nonaqueous media could be determined by this method using acid standard solutions.

Acidity and Basicity

In the Bronsted sense an acid is defined as a proton donor and a base as proton acceptor. Every acid has a conjugate base. Lewis defines an acid as a substance which accepts electrons or shares electrons with a base which is the donor of the electrons.

The Lewis acid concept is not limited to substances containing hydrogen.Lewis bases can be Bronsted bases. However Lewis concept is most appropriate for discussion of coordination compounds, oxidation-reduction reactions, and kinetics and mechanisms rather than a quantitative treatment of equilbria (E.J. King) (21). The same solvents categorized in the Bronsted sense in terms of acidity-basicity characteristics were described in six solvent classes in the Lewis sense by Popovych (2,20).A more elaborate description of Lewis acidity is found in papers by Kolthoff (27) and

Kratochvil (20). Bronsted's definition is more suited to treatment of acid-base equilibria in a continuous liquid medium, therefore this paper will place emphasis in the Bronsted description of acidity for both solvents and solutes.

Bates (31) stated that there is no single acidity and basicity scale that is valid for all solvent systems and applicable to both equilibrium and kinetic situations. Many scales exist and each scale has its own special advantages and uses. There is also no clear cut unit that is supported in the theory for the expression of the degree of acidity in all situations. Each dissociation constant measured then becomes unique with reference to the standard state of the system chosen. The choice of a different standard state for each medium suggests that there will be different acidity constants for different media. The titration curves becomes a clear illustration as to the nature of the system under study.

Popovych (2) treated the question of common standard state in terms of the medium effect or transfer activity coefficients for mixed solvents. Bates (3) explained the meaning of the medium effect in terms of the changes of the Gibbs Free energy as well. The Hammet acidity scale came about to address common acidity scales. Although this is very important for interpretation of data,and comparing solutes in mixed solvents,as well as explaining the effects of possible water contamination (18) on the dissociation constants,it will not be covered.

Solvent Properties

'Solvent effects' describes change produced in the position of equilibrium, when the nature of the solvent medium is altered. However, solvents differ widely in the following:

1. Autoprotolysis constants and Acid-base properties
2. Solvation ability
3. Dielectric constants
4. Molecular structures of the constituent molecules of the solvents and solutes as they influence each other.

Kucharsky and Safarik (18) classified non aqueous solvents into four groups, whereas Bates (22) discussed only the amphiprotic solvents in terms of the above properties. According to the former's description the four classes are as follows.

Amphiprotic, or amphoteric solvents are partially ionized into anions and cations similar to water. They tend to have high dielectric constants,and the ionic product of the liberated anion and cation on self ionisation is usually less than that of water. Alcohols belong to this group.

Protogenic ,acidic solvents are ionized but slightly amphoteric character. They freely liberate protons , tend to have high dielectric constants and their ionic product or autoprotolysis constant is usually greater than that of water. Formic, acetic,carboxylic acids belong to this group.

Protophilic basic solvents are also ionized with slightly amphoteric character. However these possess high basic properties, since they readily bind protons. These also tend to have high dielectric constants,and ionic product is less than water. Ethylenediamine, butylamine belong to this class.

Inert solvents contain no ionizable protons,have lov dielectric constants and thereby invoke much interest in terms of energetics and mechanisms since their molecular properties play a role in the acid base equilibria. Such solvents are benzene,chlorobenzene,chlorinated hydrocarbons,and hexane.

A class of solvents not mentioned by Kucharsky (22), but discussed by Harris and Kratochvil (24), are termed aprotic. These have little or no acidic or basic character, and have little or no tendency to undergo self dissociation. Such solvents include dimethyl sulfoxide,acetonitrile, and dimethylformamide. These are used to study relative basicities of amines.

Tables 1-3 shovs solvents arranged according to their acid and base properties as well as their dielectric constants. Table 3 shows only their dielectric constants and self ionisation (autoprotolysis) constants .

AUTOPROTOLYSIS CONSTANTS AND ACID BASE EFFECTS

The relative acidic and basic strength of the solute in a given solvent determines the shape of the titration curves and the sharpness of

the breakpoints (29), (Fig 1b). This strength is also a function of the acidic and basic property of the solvent as well as the dielectric constant.

The size of autoprotolysis constants (Ksh) determines whether the solvent has a tendency to interact with the solute species. Solvents with very small Ksh values react little with solute species, which is desirable in acid-base titration (24). On the other hand, when Ksh is large protonation or deprotonation of the solvent is likely to occur. This results in levelling of the strength of the acid or base and a decrease in the equilibrium constant for the sample titrant reaction. For example, in the following case

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

the reaction can only occur if the acid is brought into contact with some base which has a higher proton affinity than the conjugate base. The proton is thus partitioned between two bases and the equilibrium constant is determined by their relative affinities for the proton .

It follovs that solvents which have high acidic character (acetic) will level an acid to their strengths and similarly solvents with high basic character will level the solute base to their ovn strength. It is therefore recommended that in order to differentiate solute acid-base reactions, one should work in a solvent which is not competing with the solute for the protons. If the following reaction is considered, where B is the base and SH_2^+ is the protonated solvent,

$$B + SH_2^+ \rightleftharpoons BH^+ + SH$$

The above reaction will not proceed far to the right if the solvent has more affinity for the proton than the base.

Substances that function as an acid in one solvent do not necessarily react in the same manner in another solvent. Protogenic amphiprotic solvents are used for the titration of veak bases and protophilic amphiprotic solvents for veak acids. The solute urea is a classic example, shoving veakly basic character in water, strongly basic character in acetic acid and acidity in ammonia. Thus the activity of protons is determined by the interplay of the several acid base equilibria

involving solutes and solvents. Figures 1-8 are examples of the differentiating abilities of various solvents for particular solutes.

Those solvents which have basic properties but no acidic properties and have very small 'Ksh' such as pyridine, ethers, ketones,are quite useful in the titrations of weak acids. Figure 5 shows this effect contrasted in water and ethylenediamine (en) . Weak acids phenol and benzoic acids are shown to be differentiated in en . Figures 8,9 shows strong acids being differentiated in methylisobutylketone (m.i.k.).

Inert solvents are very useful in solvent mixtures or for titrations of acids and bases which are too weak to give end points in aqueous medium. Inert solvents are often mixed with protogenic or protophilic solvents in order to decrease the activity of the amphiprotic solvents. This produces a differentiating effect on the titration curve. Kolthoff (27) showed an example of butylamine and pyridine which are both strong bases in acetic acid solvent. Using 1 part amphiprotic acetic and 10 parts chloroform,the latter was differentiated from pyridine (27) in a titration. Kucharsky and Safarik (18) showed similar effects in acetonitrile with perchloric acid as titrant (Fig.4)

Strong bases such as alkalis, tetraalkyl ammonium hydroxide, and alkali oxides are generally insoluble in inert solvents; however, they become quite soluble in mixtures of inert and lower alcohol solvents (e.g.benzene and methanol). Many uncharged bases which are soluble in inert solvents are also too weak to be useful as a standard reagent (27). Sometimes inert solvents are preferred over amphiprotic solvents but solubility relations limit their use in pure form. In such cases the volume of reagents added during the titration is kept very small. An effective autoprototysis constant can be maintained when a small amount of amphiprotic solvent is titrated with the acid or base reagent with the reactive acid or base in an inert solvent (27). Inert solvents have large potential ranges and solute acids or bases are not levelled in them. A comparison of the potential ranges of various solvents as compared to inert ones is seen in Figure 9.

SOLVATING POWER AND EQUILIBRIA

One of the criteria for good titrimetry in a solvent is its solvating pover for given solutes. Solvents with lov dielectric constants tend to solvate less,but dielectric alone is not an adequate indication of the solvating ability of the solvent. High transfer coefficients with anions in the solvents results from poor solubilities. Coetzee (27) reported that cations are generally more solvated in vater than in acetonitrile (AN), except if the cations interact with the acetonitrile. Alkaline and alkaline earths are solvated much more readily in dimethylformamide (DMF) than in AN. Most of all in protic solvents H bonding and ion-dipole are superimposed effects that promote solvation of anions (22). Aprotic solvents tend to contribute to homoconjugation. When solvation pover of the solvent is lov the ions tend to stabilize by forming homoconjugation complexes as follows:

$$BH+ \ +B \rightleftharpoons BHB+$$

$$A- \ + \ HA \rightleftharpoons HA_2$$

If anions are small and not polarizable,they will not solvate very well and homoconjugation is thus increased.These complexes influence the shapes of the titration curves (Fig.13) as theoretically explained by Laitenen and Harris (19), and shown practically by others (7,8,9). Generally, conductivity measurements are used for the study of systems which homoconjugate (6).The solvation ability of the solvent is reflected in the polarity, degree of self ionization,and the ability to yield a conducting solution. The solvent,through interaction with the reactants and products by solvation controls the extent of the reaction between the solutes. Large dissociation constants of a solute as a result of poor solvation diminish the extent of homoconjugation.

DIELECTRIC EFFECTS

Problems in the interpretation of acidity constants arise when dielectric constants are especially lov. Here the transfer of the proton

may occur but separation of the products may not follow because of ion pair formation. Hence the dielectric constant of the solvent strongly affects the acid or base properties of a solute indirectly since interaction of solute molecules and/or ions with solvent molecules is affected. The primary acid-base reaction is between the solvent and the uncharged acid or base first, to yield the ionic compound i.e. the ionisation step and Ki is the ionisation constant.

For an acid HA,

$$HA + SH \underset{}{\overset{ka}{\rightleftharpoons}} SH_2^+ + A^- \text{ , Ki is ionisation constant}$$

For a base B,

$$B + SH \overset{Ki}{\rightleftharpoons} BH^+S \overset{Kd}{\rightleftharpoons} BH^+ + S^- \text{ , Kd is dissociation constant}$$

The second stage is the dissociation of the ion-complex to form free ions at infinite distance apart and the equilibrium constant of this step is the dissociation constant Kd. However the acid constant of the reaction Ka is defined by the equation:

$$Ka = \frac{KiKd}{1 + Ki}$$

Dielectric constants reflect the capacity of a solvent to separate the ions in the dissociation step. A lov dielectric constant suggests a large Kd. The higher dielectric solvents have solute solvent interactions through electrostatic attraction, therefore separation is easier.

This process of proton solvation and ion separations requires work. Thus the free energy for these steps is derived from electrostatic effects and is described by the Born equation (3,27,21). The nonelectrical contribution to free energy, ΔG° nonelec comes from other factors such as bond-dissociation energies and changes in translational, rotational and vibrational energies as well as specific solvation effects.

$$\Delta G^{\circ} = \Delta G^{\circ}\text{elec} + \Delta G^{\circ}\text{nonelec} = -RT \ln K$$

$$K = K \text{ nonelec} \cdot K \text{ elec}$$

Kolthoff (27) and King (21) both shoved that the free energy difference for the dissociation of a mole of HB in solvent 1 and solvent 2 is inversely related to the dielectric constant, which is the basis of the Born equation,

$$\text{Eqn (4)}.. \quad (\Delta G^{\circ}\text{elec})_2 - (\Delta G^{\circ}\text{elec})_1 = -\frac{Ne^2}{R} \quad \frac{1}{r_{H^+}} + \frac{Z_B^2}{r_B} - \frac{Z_{HA}^2}{r_{HA}}$$

$$-\frac{1}{D_2} - -\frac{1}{D_1}$$

where z1 = charge, r_i=radius and D_i = Dielectric constent

When ΔG nonelectric was ignored and Kolthoff and Bruckenstein (27) considered the acid or base strength of two solvents 1 and 2 to be equal then the following relation held:

$$\text{Eqn (5)}.....\Delta G_2^{\circ} - \Delta G_1^{\circ} = -RT \ln (K_{HB})\ 2 \ /\ (K_{HB})1$$

Eqn (4) and (5) show that the log of the dissociation constants in two acids are inversely proportional to the dielectric constant. It follows that one can predict how the charge type of an acid affects the dissociation constants. However the radius of the ions and the activities of the ions as well as the uncharged acid or base in the solvent are not equal in all solvents. The approximation is valid for two solvents of very similar acid and base properties, and the assumption that ΔG nonelec is independent of solvent. Prediction of the difference in pK values of two acids of same charge can be made if the nonelectrical effects is ignored (27).The acidity constant of an acid changes when one solvent is substituted by another, as seen by the relation.

$$\ln \frac{K_{A1}}{K_{A2}} = \frac{e^2}{2KT_r} \quad (\frac{1}{D_1} - \frac{1}{D_2}) \quad (2Z_r - 1)$$

where K=Boltzman const., K_{A1} K_{A2} are dissociation constants

If assumptions are made that all radii of acid and base are equal, comparisons can be made. For example,when acid strengths were compared with

reference to acetic acid in water and methyl Isobutylketone (m.i.k.)(3),it was found that salicylic acid was about 50 times as strong relative to acetic acid in (m.i.k) as in water, although phenol and benzoic acid relative to acetic acid were unchanged in the two solvents. This increase in acid strength was related to nonelectrical effects such as stabilization due to H-bonding. The competition between oxygen in the solvent and oxygen in the COO- group for the H was smaller in m.i.k. Thus the nonspecific interaction of the solvents play a role in the acid-base properties.

Anionic acid has a larger decrease in strength than an uncharged acid when the dielectric constant is decreased. The Born relation holds best for high dielectric solvents. In lov dielectric solvents ion pair formation is predominant and ion dipole, dipole-dipole interactions,and H-bonding are important.

Solvents with lov dielectric constants often indicate ion association and some homoconjugation, since solvation is poor as well. In a solvent with lov dielectric there is insufficient free energy to perform the work necessary to separate the ionic associated pair.Thus ion pair formation becomes more influenced by molecular properties of the solute and solvent. Hydrogen bonding becomes more important. Above dielectric constants of 40, ion pair formation and dissociation of ion pairs are not considered a problem.

Dielectric constants have been shown to affect the dissociation constant of an ion pair when mixtures of solvents are made to control the dielectric. A typical example by Fuoss and Krauss is quoted by Kolthoff and Bruckenstein (27). Water dioxane mixtures are used to determine the dissociation constants of tetraisoamyl ammonium nitrate. It was found that the pK values rapidly increase when the dielectric constants was less than 6.

It is also known that the change in dielectric constant of two equilibria will depend on the charge type of the acid-base conjugate pair. The primary effect of a decreased dielectric constant is that it seems to make the separations of anions and cations more difficult. If the acid is a cation like NH_4^+ ion the dissociation process does not require the creation of new charges and so the equilibria is not greatly affected. Similarly, for an anionic acid HB^- dissocation decreases when there is more coulombic attraction between the base and the proton.

$HB^+ \rightleftharpoons B + H^+$ ....eq 6...is unaffected by low dielectric

$HB \rightleftharpoons B^- + H^+$ ....eq 7...is affected by low dielectric

$H\bar{B} \rightleftharpoons B^{-2} + H^+$ ....eq 8.. is affected to the right by low dielectric

Thus in eq 6 the reaction shifts to the right,in eq 7 the reaction shifts to the left and eq 8 the reaction shifts to the right, because of increased coulombic attraction based on charge. A summary of these effects combined with basicities are seen in table 5.

Similar effects were studied by Sakamoto et al (6) who used conductometry and potentiometry to study acid-base equilibria of a variety of acids in acetylacetone. The autoprotolysis constant was estimated potentiometrically with a glass and calomel electrodes to be 19.3. Acetylacetone (2,4-pentanedione) is normally used as a chelating agent). It was described as protic with a dielectric constant of 27.2 at 25°C. Anions are solvated through hydrogen bonding based on the enol form of the solvent; cations are not as strongly solvated. In the determination of the dissociation equilibria in this solvent, the authors considered three types of equilibria of a weak acid HA .

$HA \rightleftharpoons H^+ + A^-$ $K(HA) = [H^+]\,[A^-]\,f^2/[HA]$

$A^- + HA \rightleftharpoons HA_2^-$ $K(HA_2^-) = [HA_2^-]/[A^-][HA]$

$HA + HA \rightleftharpoons H^+ + HA_2^-$ $K(2HA) = K(HA).\ K(HA_2^-)$

where K(HA), $K(HA_2^-)$ and K(2HA) are the dissocation,homoconjugation and overall dissociation constants respectively. Acids considered were 2, 5 dichlorobenzene sulfonic, p-toluenesulfonic, methanesulfonic and picric acids.

The results indicated a decrease in molar conductivities with concentration of acids and hence they suggested homoconjugation occured with methanesulfonic (pK 4.0) and p-toluenesulfonic (pK =3.7). For 2,5

dichlorobenzene sulfonic acid pK(HA) was 5.1 and $K(HA_2^-)$ was 8.4×10^2. Picric acid did not homoconjugate.

Mixtures of these acids were then titrated with their tetralkylammonium salts which is completely dissociated in this solvent. A summary of their findings shown in table (6) illustrates several principles of solvent effects on dissociation equilibria. The dissociation constant in acetylacetone was compared to two other aprotic solvents having slightly acidic properties. They attributed the small pK(HA) values in acetylacetone as compared to propylene carbonate and acetonitrile, to hydrogen bonding ability of the acetylacetone towards the anions based on its tautomeric enol form. They suggested the basicity of acetylacetone is weaker than the two other solvents.

Most ketones have been known to have more basic than acidic properties (24). Acetylacetone shows K(HA-) values almost equal to the other aprotic solvents. This was also attributed to hydrogen bonding in the enol form which reduced both the solvent's acidity and basicity. Thus in acetylacetone, the undissociated acid are more strongly hydrogen bonded to the less acidic solvent acetylacetone and so homoconjugate their anions for stability. Acetylacetone is less basic and less acidic as well for the study of dissociation of weak acids.

EFFECTS OF MOLECULAR PROPERTIES OF SOLVENTS

Although Bates (3) summarized the combined effects of dielectric constants, acid-base charge type, and decreased solvent basicity on the pKa of an acid in a solvent, he did not discuss molecular effects. He limited his paper to amphiprotic solvents of high dielectrics. Other studies shoved that, especially in solvents with more aprotic and inert properties as well as lov dielectric constants, molecular features play a large role in the relative basicities, in particular solvents. Acidity and basicity orders are determined for different solvents, and solutes. These effects are manifested in the shapes of the titration curves as well as in the pKa values.

The basicity order of several organic bases was studied recently by Kilic et al (9). The factors influencing the basicity of Schiff Bases in

nitrobenzene as solvent was studied by potentiometric titrations. Schiff bases are considered weak and nitrobenzene fairly inert(dielectric of 36). The titration was performed with perchloric acid. Titration curves were s-shaped. The basicities of the Schiff bases were influenced by several factors such as aldehyde component, amine function, methylene groups, one hydroxy group, two hydroxy groups and alpha and beta amino substitutions. These groups influenced the shapes of the titration curves as well as the pKa values. Examples of the influence of the hydroxyl groups is seen in the curves in Figs.10 & 11. These authors have attributed the basicities to A) inductive effects of substituted aryl and allkyl substituents, B) steric effects, C) solvent dipole movement, D) dielectric constant, acidity and basicity and E) hydrogen bonding and resonance effects.

Gunduz et al (8) studied the basicity order of aniline, N-alkyl and N-aryl substituted anilines and pyridine in nitrobenzene solvent, in order to distinguish which structual effects influenced the relative basicity and to what extent it did so. They studied these effects by potentiometry. Although these bases were studied in other media (32), the authors claimed that this order was not determined in nitrobenzene which gave good s-shaped curves and no homoconjugation. They found that the overall basicity order was

NH_3 > Pyr> $PhNEt_2$ > $PhNMe_2$ > PhNHEt $PhNHMe$ > $PhNH_2$ > Ph_2NH >Ph_3N

N-Alkyl substituted anilines were more basic than aniline and N-aryl substituted anilines less basic than aniline. However, in dimethyl sulfoxide, $PhNH_2$> Pyr in basicity. There were also increase in the basicity of aniline with the increase in number and size of substituents. A plot of number of hydrogen atoms versus half neutralization present gave a straight line. They attributed the increased basicity to greater polarizability of the lone pair of electrons on nitrogen. Earlier work by Benoit etal (28), using trifluoromethanesulfonic acid as titrant showed different results in dimethylsulfoxide solvents. They measured the dissociation constants of the conjugate acids of anilines,along with heats of solutions and heat of neutralization of the bases. The order was different in the gas phase and opposite in water. They ascribed this difference to heat of solution and H-bonding being more important than size of R substituent.

In nitrobenzene solvent Gunduz et al (7) looked at the basicity order of aliphatic amines using potentiometric titration and perchloric acid

as the titrant. The curves were quite s-shaped and stochiometric. There was again no homoconjugation. A comparison of the same experiments in nitrobenzene-light petroleum solvent mixtures gave the same order, only methylamine showed a different order. Basicity decreased with the increased size of the alkyl group, quite unlike aniline. Evidently these orders are unique to the solvent media. Butylamine is more basic than the branched chain butylamines. There was no theoretical explanation for ethylamines being a stronger base than methylamines.

Daniele et al (5) used cyclic voltammetry to evaluate solvent basicity. Nitromethane, acetonitrile, tetrahydrofuran, 1,2- dimethoxyethane, dimethylformamide dimethysulphoxide and pyridine were determined using electrogenerated anhydrous perchloric acid . Ion pair formation tended to complicate matters by low proton activity and cause more difficult reduction of HS+ species and an apparent higher basicity of the solvent. Their data compared well with the literature as well as with potentiometric data which was obtained on adding $HClO_4$ in different solvents to the bases. E1/2 values are affected by the nature of the medium. The reduction of the acids conjugated with pyridine morpholine and piperidine occured at increasingly negative values as the basic character of the solvent increased. H-bonding was also suggested to be stronger the more basic the solvent.

Ugo, Paolo et al (4) studied hydrogen bond formation in polar organic solvents using cyclic voltammetric techniques. Hydrogen bonding conditions the proton activity in a given organic solvent. Because acetonitrile is poorly H-bonding it was used as a reference solvent. A change in basic species was easily monitored by looking at the effect on proton activity.

$H+/H_2$ redox couple was measured after mixing reference solvent (R) with increasing fractions of more basic solvents (S) such as 1,2 dimethoxyethane,DMF, tetrahydrofuran,THF, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine (pyr). Freshly prepared perchloric acid titrant was used. The relative basicities of solvent to reference solvent was seen in the dissociation equilibria for the basic solvent. Results showed that all solvents form Hydrogen Bonded species of HS_2^+ type and higher order association products were not formed even by the more basic solvents. Both DMF and Pyr had high K_1 and K_2 whereas, for DMSO K_2 was much greater than K_1. They suggested steric hindrance was contributing to the

dissociating constants,and that the ranking of basicity must be exercised with caution as to which criterion must be used. If ranked by H-bonding ability DMSO would be more basic than Pyr. If steric hindrance is considered as well DMSO would be less basic than pyridine.

Since their K_1 constants increased with relative basicity order of solvents, and K_2 did not increase with solvent basicity they suggested other effects were effective in formation of H-bonded solvent association species. Increased basicities with morpholine and piperidine was observed with a change in solvent from pyridine to DMSO. Heteroconjugated complexes of the type $HBS^+$was suggested with S=DMSO, because of higher tendency to H-bonding.

They concluded that the strength of base when used as a solvent differs from its intrinsic basicities. Basicity data should be considered in terms of whether the solvent is used as the medium or as the basic titrant dissolved in another medium with little tendency to hydrogen bonding.

CONCLUSION

Equilibria are complex interplay of many factors, thorough discussion of which has and will continue to fill many books. The properties of solvents explain the effects on the equilibrium constants, the shapes of titration curves, and the acid base behaviour of the reactants and products.The main points discussed in this paper are summarized:

1. Weak acids up to a pKa of 11,and weak bases slightly ionized in water may easily be titrated in an appropriate nonaqueous solvent.

2. Potentiometry,voltammetry,and spectrophotometry are commonly used for end point detection.

3. Calculation of pKa is best performed by iterative techniques, especially for solvents of low dielectric constant and poorly solvated solutes.

4. To avoid levelling effects neutral solvents are chosen.

5. Mixtures of acids are normally differentiated in nonaqueous solvents otherwise impossible in water.

6. Homoconjugation will occur in solvents of low dielectric constant and poor solvating power. This is apparent in titration curves.

7. Consideration must be given to changes in activity coefficients in various solvents, especially in basic and neutral solvents, in the determination of pK.

8. Above all the relative basicities of solutes are solvent dependant, and structural properties of the molecules influence their behaviour in the solvents. A large part of nonelectrostatic effects on equilibria, which is neglected by the Born Equation, is seen in the H-bonding and steric influence of the molecules.

The fundamentals of energetics as it relates to equilibria, and methods of studying equilibria were discussed, along with the recent developments in the calculation of pKa. Solvating power, dielectric constant, and functional group effects in solute basicities, as well as charge effects of acids in solvents, influence the pK. Each system responds uniquely to its own conditions.

TABLE 1

Characteristic Properties of the Individual Solvent Groups

Group	I	II	III	IV	V	VI	VII	VIII
Dielectric constant	+	+	+	+	-	-	-	-
Protogenia	+	+	-	-	+	+	-	-
Protophilia	+	-	+	-	+	-	+	-

TABLE 2

Dielectric Constants of Solvents

Solvent	Dielectric constant	Group	Solvent	Dielectric constant	Group
H_2O	81.0	I	HI	2.9	VI
H_2SO_4	84.0	II	CH_2COOH	6.4	VI
HF	84.0	II	NH_2	17.0	VII
HCOOH	58.0	II	CH_2NH_2	10.0	VII
N_2H_4	54.0	III	C_5H_5N	12.0	VII
CH_3OH	31.0	VI	$C_5H_5NH_2$	7.2	VII
C_2H_5OH	24.2	VI	C_4H_6	2.3	VIII
$isoC_5H_{11}OH$	5.7	V	C_6H_5CI	5.8	VIII
HCI	4.6	VI	C_5H_{12}	1.8	VIII
HBr	3.8	VI			

Solvents of Group IV do not exist.

Ref. (18)

TABLE 3

Properties of Several Nonaqueous Solvents

Solvent	pK_s	Dielectric constant
Acetic acid	14.5	6.1
Acetone	----	20.7
Acetonitrile	32	36.0
Ammonia	29.8	16.9
Benzene	----	2.3
Carbon tetrachloride	----	2.2
Chloroform	----	4.8
Dimethylformamide	18.0	36.7
Dimethylsulfoxide	33	46.6
Ethanol	18.9	24.3
Ethylenediamine	15.2	12.5
Formic Acid	6.2	57
Methanol	16.5	32.6
Methylisobutyl ketone	----	13
2-Propanol	20.6	18.0
Pyridine	----	12.0
Toluene	----	2.4
Water	14.0	78.5

TABLE 4

Approximate potential ranges measured with glass and calomel electrodes in twelve solvents [4].

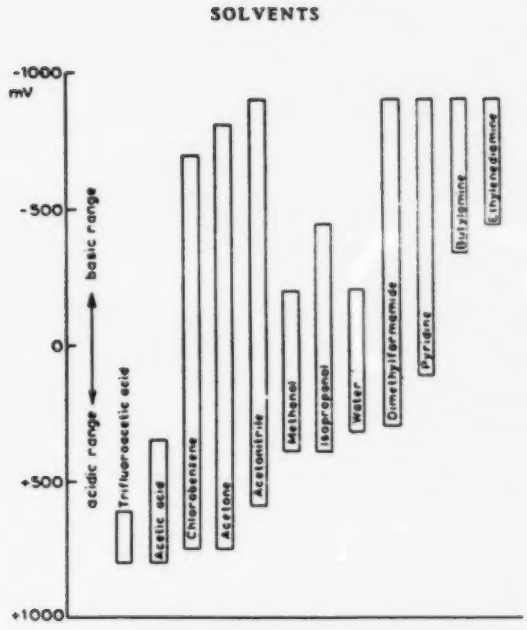

TABLE 5

Qualitative Effects of a Change in Solvent Properties on Protolyic Equilibria

$$HA + SH \rightleftharpoons SH_2^+ + A$$

z	Acid-base charge type	Decreased solvent dielectric constant	Decreased solvent basicity
0	A+,B°	(minor effect)	(pK increases)
-1	A°,B-	(pK increases)	(pK increases)
-2	A-,B-	(pK increases)	(pK increases)

*A=acid; B=base

TABLE 6

pK(HA) and K(HA_2^-) values of some weak acids in acetylacetone, propylene carbonate and acetonitrile

	Acetylacetone		Propylene carbonate[3]		Acetonitrile[3]	
	pK(HA)	pK(HA_2^-)	pK(HA)	pK(HA_2^-)	pK(HA)	K(HA_2^-)
2.5-Dicnloro-benzenesulfonic	5.1	600	4.9	470	6.2	300
p-Toluenesulfonic	6.7	1000	6.4[5]	1700[5]	8.0[5]	790[5]
Picric	7.7	~0	9.2	~0	11.0	2
Wethanesulfonic	7.9	7800	8.3	2500	10.1	3000

(The three acid types can be differentiated by titration in dimethyl-formamide. Mineral acids cannot be differentiated from carboxylic acids in ethylenodiamine (they are equally strong in this medium) but they can be differentiated as a group, from phenols.)

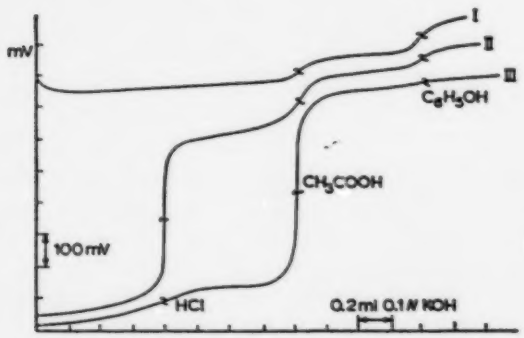

Fig. 1 - Titrations with 0.1 N potassium hydroxide solution in ethanol, using glass and calomel electrodes, of a mixture of a strong, a weak, and a very weak acid (hydrochloric acid, acetic acid, and phenol) in ethylenediamine (curve I), dimethylformamide (curve II), and water (curve III) [18]. (After Kucharsky (18)).

Neutralization Titrations

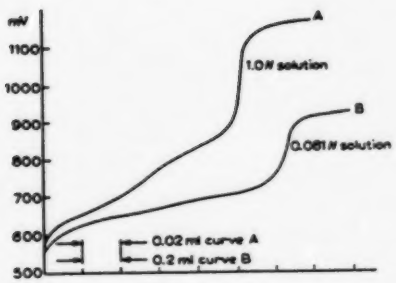

Fig. 2 - Titrations of 0.1 meq of phenol in pyridine[29] with 1.0 N and 0.081 N tetrabutyl-ammonium α-methylethoxide solutions in isopropanol, using glass and calomel electrodes. (After Lagowski (22)).

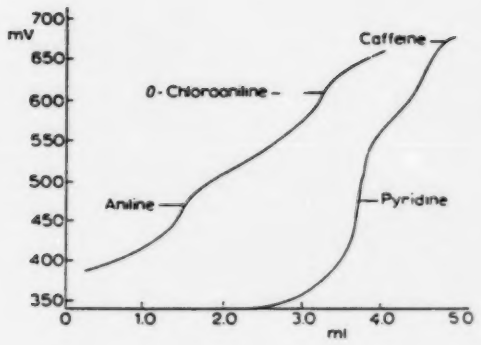

Fig. 3 - Titrations of o-chloroaniline in the presence of aniline, and of caffeine in the presence of pyridine, in acetonitrile [27], with 01. N perchloric acid solution in anhydrous acetic acid, using glass and calomel electrodes. (After Kucharsky (18)).

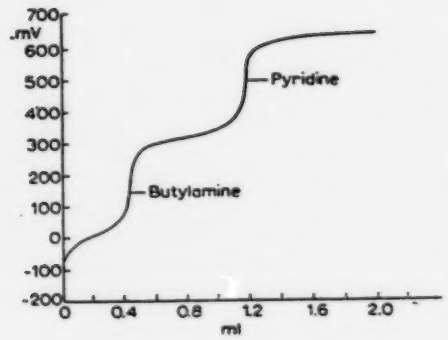

Fig. 4 - Titration of pyridine in the presence of butylamine, in acetonitrile[27] with 0.1 N perchloric acid solution in dioxan, using glass and calomel electrodes. (After Kucharsky (18)).

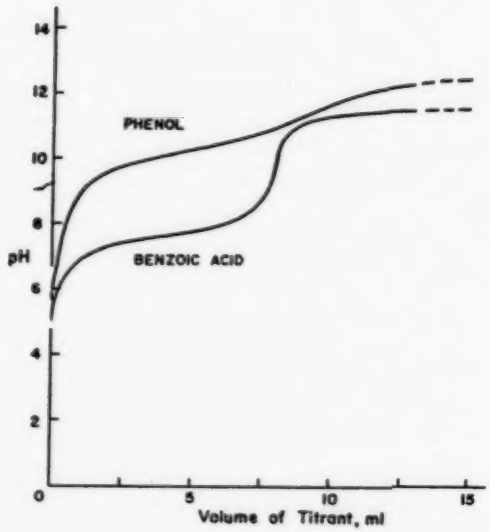

Fig. 5 - Titration curves for the titrations of benzoic acid and phenol in ethylenediamine (a strongly basic solvent). The titrant was 0.2 F sodium aminoethoxide dissolved in a mixture of ethanolamine and ethylenediamine. The use of a much more basic titrant-solvent system enhances the acidity of benzoic acid and phenol and makes the titration curves more sharply defined than in Figure 6. Although expressed in different units, the size of the vertical scale is the same as in Figure 6. (After Peters et al (25).

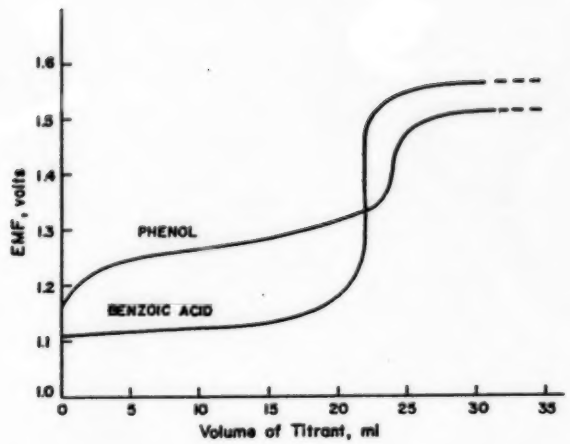

Fig. 6 - Titration curves for the titrations of benzoic acid and phenol in water with a 0.5 F sodium by droxide solution. (Redrawn, with permission, from the paper by M.L. Moss, J.H. Elliott, and R.T. Hall: Anal. Chem., 20: 784, 1948.) After Peters et al (25).

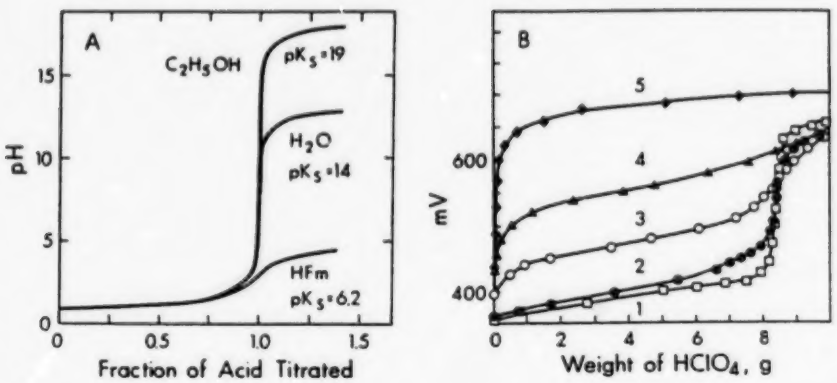

Fig. 7 - (A) Calculated titrations of 0.1 M solutions of the strongest possible acid with the strongest possible base in ethanol, water, and formic acid. (B) Titrations of amines of varying base strength with perchloric acid in glacial acetic acid. (The ordinate is a millivolt scale instead of pH to indicate that actual pH is unknown in this system.) pK_A values for H_2O as solvent: (1) Aniline, 9.4; (2) p-bromoaniline, 10:1; (3) o-chloroaniline, 11.2; (4) p-nitroaniline, 12:1; (5) blank, (After Harris & Kratochvil (24)).

Thus acid-base titrimetry in water cannot resolve such a mixture.

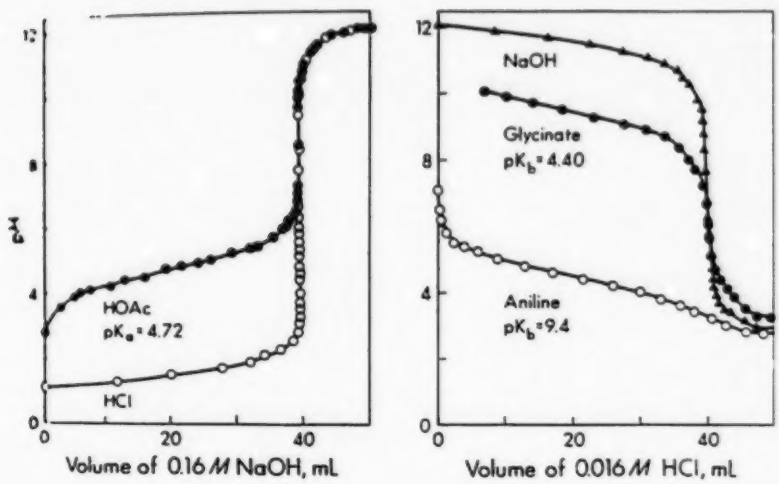

Fig. 8 - Curves for the titration of hydrochloric acid and acetic acid with sodium hydroxide and for the titration of sodium hydroxide, sodium glycinate, and aniline with hydrochloric acid. (After Harris & Kratochvil (24)).

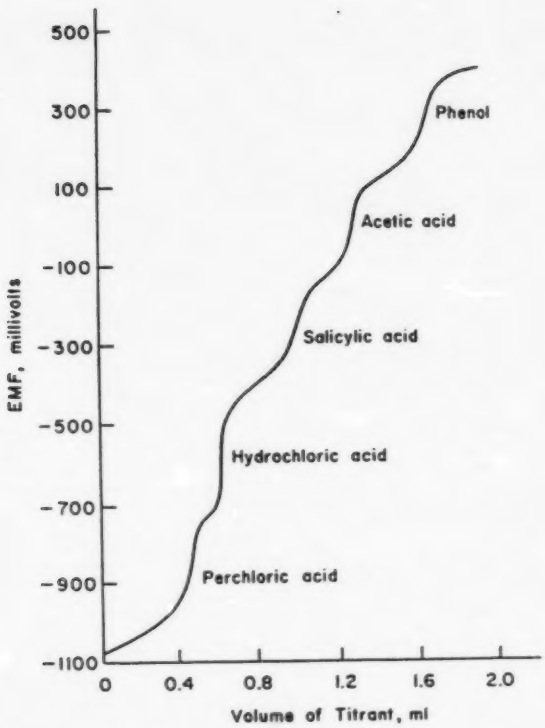

Fig. 9 - Titration curve drawing the resolution of a mixture of strong ang weak acids in methyl isobutyl ketone. The titrant was tetrabutylammonium hydroxide in isopropanol. A glass indicator electrode and a platinum wore reference electrode were used. (After Peters et al (25)).

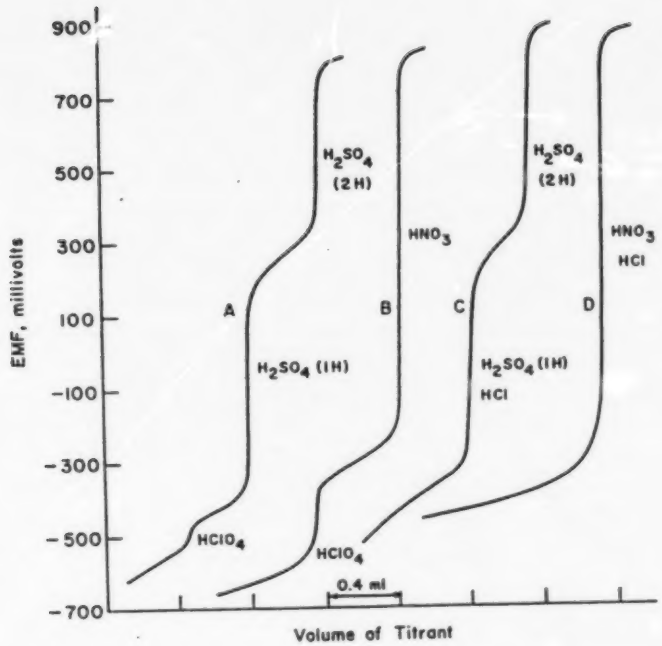

Fig. 9a. - Titration curves for various mixtures of strong acids in methyl isobutyl ketone with 0.2 F tetrabutylammonium hydroxide (in isopropanol) as the titrant. A glass indicator electrode and an aqueous saturated calomel reference electrode were employed to measure the cmf values. (Redrawn, with permission, from the paper by D.B. Bruss and G.E.A. Wyld: Anal. Chem., 29:232,1957). (After Peters et al (25)).

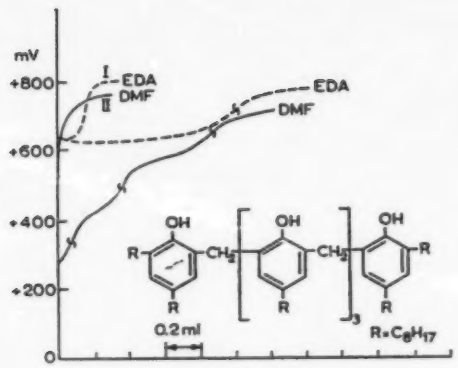

Fig. 10 - Titrations of a polyphenolic compound in ethylenediamine (EDA) and dimethylformamide (DMF)[13] with 0.2 N potassium hydroxide solution in ethanol, using glass and calomel electrodes. Curves I and II correspond to the titrations of pure solvents. (After Kucharsky (18)).

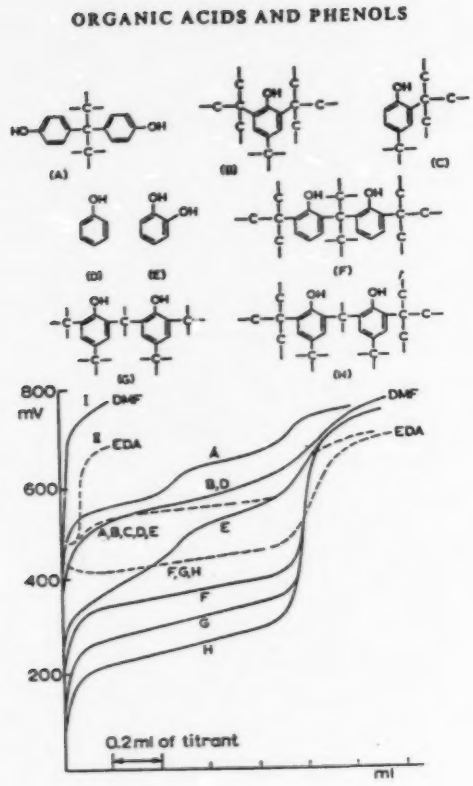

Fig. 10a. - Titrations of phenolic compounds in dimethylformamide (DMF, solid lines) and ethylenediamine (EDA, dash lines)[13] using glass and calomel electrodes. Curves I and II correspond to the titrations of pure solvents. Those substances dissolved in dimethylformamide were titrated with 0.1 N tetrabutylammonium hydroxide solution in isopropanol, and those dissolved in ethylenediamine with 0.1 N potassium hydroxide isolution in ethanol. (After Kucharsky (18)).

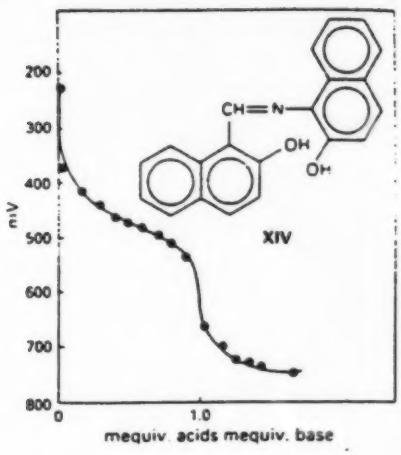

Fig. 11 - Titration curve of salicylidene-2-hydroxy-1-naphthylamine (XIV) in nitrobenzene. (After Gunduz et al 1986. (7)).

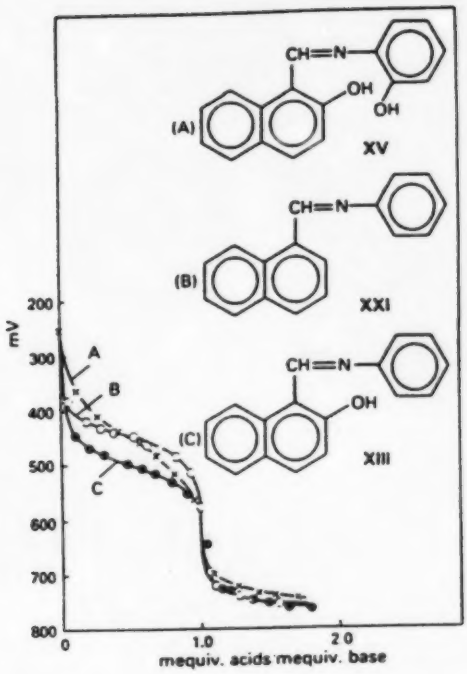

Fig. 11a - Influence of Hydroxy groups on the basicities of congener Schiff bases. (After Gunduz et al 1986 (7)).

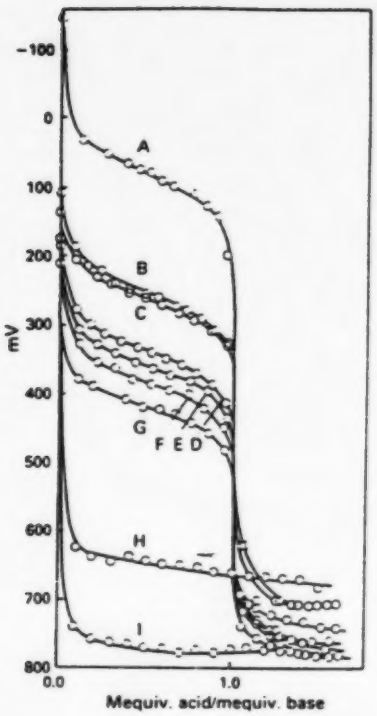

Fig. 11b - Potentials versus mequiv. acids/mequiv. base. Base: A. amonia: B, pyridine: C, N,N-diethylaniline; D, N,N-dimethylaniline; E,N-ethylaniline; F,N-methylaniline; G, aniline; H, diphenylamine; and I. triphenylamine. (After Gunduz et al 1986 (7)).

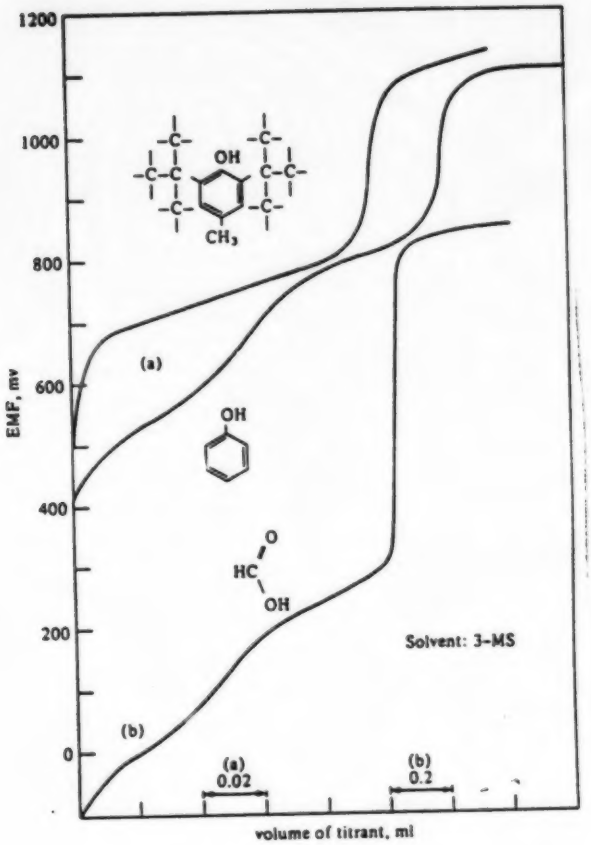

Fig. 12 - Titration of acids in 3-methylsulfolane with tetrabutylammonium hydroxide. The extra inflection in the titration of phenol (a) and formic acid (b) is caused by homo-conjugation. In the titration of 2,6-di-t-butyl-4-methyl phenol homoconjugation is prevented by steric effects of the bulky groups ortho to the phenolic OH. (After Fritz (23)).

REFERENCES

1. Garrels, R. and Christ, C.L., Solutions Minerals and Equilibria Ch. 1., Freeman Cooper , 1965

2. Popovych,O., Estimation of Medium Effects for Single Ions in Nonaqueous Solvents, Critical Reviews in Analytical Chemistry, Vol 1. 1970

3. Bates, R.G., Chapt 2, Reference 27.

4. Ugo, Paolo; Daniele, Salvatore; Mazzocchin, Gian Antonio and Bontempelli, Gino., Acid-base equilibria in organic solvents, Journal: Anal. Chim. Acta, Vol. 173, pps. 149-56.

5. Daniele, Salvatore; Ugo, Paolo; Mazzocchin, Gian Antonio and Bontempelli, Gino, Acid-base equilibria in organic solvents, Journal: Anal. Chim. Acta, Vol. 173, pps. 141-8.

6. Sakamoto, Ikko; Masuda, Kaoru; Okazaki, Satoshi and Fujinaga, Taitire, Acid Base Equilibria in Acetylacetone, Journal: Bunseki Kagaku, Vol. 31, pps. 1982, E49-E52 and ISSN, pps. 0525-1931.

7. Gunduz, Turgut; Gunduz, Necla; Kilic, Esma and Kenar, Adnan, Titrations in Nonaqueous Media. Part 3., Analyst (London), Vol. 111, No. 9, 1986, pps. 1103-5.

8. Gunduz, Turgut; Gunduz, Necla; KIlic, Esma; Kenar, Adnan and Cetinel, Gulay, Titrations in Nonaqueous Media. Part 2, Analyst (London) Vol. 111, No. 9, 1986, pps. 1099-101.

9. Kilic, Esma and Gunduz, Turgut, Titrations in Nonaqueous Media. Part 1, Analyst London) Vol 111, No. 8, 1986, pps. 949-53.

10. Papanastsiou, G; Ziogas, I and Moumtzis, I., Acid-base Equilibria in Ternary Water/Methanol/Dioxane Solvent Systems, Anal. Chim. Acta Vol. 186, 1976 pps 213-21.

11. Halliday, Colin G., Kelly, Theresa J and Leonard, Michael, A., Equivalence-Point Location in the Titration of a Weak acid with Sodium Hydroxide Solution: A Comparison of Photometric and Potentiometric Methods, Analyst, 1984, 109 (10); 1309-11.

12. Castillo, Carlos S., Micolta, Germania S., and Grajales, Mario, T. An Alternative Method for the Determination of PKa, Journal of Chemical Education, 1984, Gl, (12); 1067.

13. Petho, Gabor and Burger, Kalman, The Use of the Half Neutralization Point In the Potentiometric Determination of Weak Bases in Water, ACTA Chimica Academiae Scientiarum Hungaricae, 1981, 108, (2); 161-5.

14. Avdeef, Alex, Kearny, Diane L., Brown, Jessica A., and Chemotti, Alfred R., Bjerrum Plots for the Determination of Systematic

Concentration Errors in Titration Data, Analytical Chemistry, 1982, 54, (13) 2322-6.

15. Velinov Georgi; Budevsky, Omortag, Potentiometric Methods for the Determination of Autoprotolysis Constants of Amphiprotic Nonaqueous Solvents, Part 2., J. Electroanal. Chem, 71 (1976) 317-324.

16. Petho,G and Burger,K., The use of Half Neutralization Point in the Potentiometric Determination of Weak Bases in Water, Acta Chimica Academiae Scientiarum Hungaricae, Tomus 108 (2), pp.161-165, (1981)

17. Kratohvil,B. Titrations in nonaqueous solvents, Analytical Chemistry reviews, VoL. 52, Page 151R, April 1980; Vol 50.153R, April 1978; Anal Chem. 1982,54,105R-121R.

18. Kucharsky J. and Safarik, L. Titrations in Non-Aqueous Solvents, Elsevier Publishing Company, 1965.

19. Laitenen, H.A. and Harris, W.E., Chemical Analysis, Second Edition, Chapters 2 and 4, McGraw Hill, 1975.

20. Kratohvil,B., Oxidation Reduction Reactions in Nonaqueous Solvents. Record of Chemical Progress, Vol. 27, No.4, December 1966.

21. King, E.J., International Encyclopedia of Physical Chemistry and Chemical Physics, 1965, Vol. 4, Acid-Base Equilibria.

22. Lagowski, J.J. Chemistry on Non-Aqueous Solvents Principles and Techniques .Vol 1, Academic Press, 1966.

23. Fritz,J.S., Acid Base Titrations in Nonaqueous Solvents, 1973, Allyn Bacon, Boston.

24. Harris, W.E. and Kratochvil, B., An Introduction to Chemical Analysis. Saunders, Publishing, 1980.

25. Peters, D.G., Hayes, J.M., Hieftje, G.M., Chemical Separations and Measurements, Saunders, 1974.

26. Skoog, D.A. and West, D.M., Fundamentals of Analytical Chemistry. Holt Rinehart, Third Edition, 1976.

27. Kolthoff, I.M., Elving, P.J. Treatise on Analytical Chemistry, Part 1, Vol. 1, Theory and Practice, Interscience Encyclopedia Inc. 1977, New York.

28. Hartley, F.R. Burgess,C. Alcock,C., Solution Equilibria, 1980, John Wiley.

29. Svehla,G., Automatic Potentiometric Titrations, 1977, Oxford Univrsity Press,Ch 8.

30. Rosotti, FJ. Rosotti,H., Determination of Stability Constants 1961, Mcgraw Hill,London

31. Bates, R.G., Bulletin Soc Chim Belges, Vol 84, 1975, 1139-1157.

32. Benoit,R.L., Mackinnon,M., Bergeron,L., Basicity Order of N-Substituted Anilines and Pyridines in Dimethyl Sulphoxide, Can J.Chem. 1981, 59, 1501.